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by

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# Electronic Structure of Fullerene Tubules

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## ABSTRACT

Recent reports suggest that graphitic tubules with diameters on the order of fullerene diameters have been synthesized. Such small-diameter tubules should have electronic properties related to those of two-dimensional graphite. We demonstrate by comparison with results from a first-principles, self-consistent, all-electron Gaussian-orbital based local-density functional approach that an all-valence tight-binding model can be expected to give a reasonable description of the electronic states of these tubules. In analyzing both high-symmetry tubules and lower-symmetry chiral tubules, we see that a relatively high carrier density could be expected for many of these structures.

## INTRODUCTION

Recent developments in synthetic techniques have allowed the synthesis of macroscopic amounts of the all-carbon fullerenes $C_{60}$ and $C_{70}$, [1] and the availability of these materials has led in turn to an explosive increase in research efforts concentrating on understanding the fullerenes. Several workers have speculated on the possibility of obtaining small-diameter all-carbon tubules with transverse dimensions on the scale of the molecular fullerenes. [2–4] Work on carbon fibers [5,6] has demonstrated that tubular graphitic filaments can be synthesized with filament diameters as small as 10 nm. Recently, Wang and Buseck [3] have reported observations of elongated ellipsoidal structures in transmission electron microscopy images of fullerene materials, which were interpreted as larger all-carbon fullerene cages containing roughly 130 carbons. Chai, *et al.* [4] have discussed the possibility that fullerenes containing multiple metal atoms may be extended prototubular structures such as those seen by Wang and Buseck. Iijima [7] has presented preliminary work that suggests that graphitic tubules with diameters as small as 2.2 nm can be produced using an arc-discharge evaporation method similar to that used for fullerene synthesis, with small carbon needles grown on one of the electrodes.

Herein is a preliminary report of our work analyzing the electronic structure of fullerene tubules. First we present results for the electronic structure of a high-symmetry fullerene tubule using a first-principles, self-consistent, all-electron Gaussian-orbital based local-density functional approach. We then compare results we obtain for the same tubule using a valence tight-binding approach, and find that the full-valence tight-binding approach can give an reasonable description of the one-electron energy levels with appropriate parameterization. We finally examine a sample chiral tubule similar to those suggested by Iijima's work, and discuss how the electronic states should affect the properties of these materials.

## TUBULE STRUCTURE

As noted by previous workers, a model for a graphitic tubule is that of rolling up a single layer of graphite in its honeycomb lattice into a cylindrical tubule with constant diameter. We can thus visualize the graphitic tubule as a conformal mapping of the two-dimensional honeycomb lattice (depicted in Figure 1) to the surface of a cylinder.

We can then see directly by inspection of Figure 1 that the proper periodic boundary conditions can only be satisfied if the circumference of the cylinder maps to one of the Bravais lattice vectors for the graphite sheet. Thus each real lattice vector of the two-dimensional hexagonal lattice (the Bravais lattice for the honeycomb) defines a different way of rolling up the sheet into a tubule. The point group symmetry of the honeycomb lattice will make many of these equivalent, however, so truly unique tubules are only generated using a one-sixth irreducible wedge of the Bravais lattice.

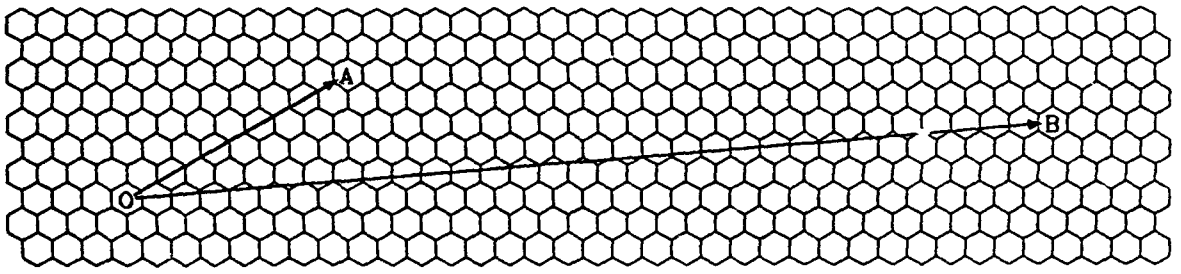


Figure 1. Two-dimensional graphite lattice structure. Line segments $OA$ and $OB$ represent two lattice translation vectors for the hexagonal lattice.

Furthermore all tubules generated by such a conformal mapping must have translational periodicity. In our conformal mapping, we choose a real lattice vector (although not necessarily a primitive lattice vector) to map to the circumference of the tubule. The perpendicular direction then maps to the tubule axis. Consider the primitive reciprocal lattice vectors of the two-dimensional hexagonal lattice. These vectors are by construction each perpendicular to one of the primitive real lattice vectors. The perpendicular to a real lattice vector is then proportional to within a scalar constant to an integer multiple of the primitive reciprocal lattice vectors. For the hexagonal lattice there exist real lattice vectors also proportional to the primitive reciprocal lattice vectors to within a scalar constant; therefore we will always be able to find a real lattice translation vector that maps to the tubule axis direction. Thus all such tubules must have translational periodicity.

The base fullerene, $C_{60}$, has a soccer-ball structure (a truncated icosahedron) formed from 12 pentagons and 20 hexagons. [8–11] Experimental evidence [9,12] implies that the larger fullerene, $C_{70}$, has a $D_{5h}$ structure that can be constructed by orienting the $C_{60}$ along one of its $C_5$ axes, and then inserting 5 new hexagons by equatorially adding a planar ring of 10 carbon atoms while simultaneously rotating the two caps with respect to each other. As discussed by several workers, an extended structure can be formed by continuing to add such rings, each one rotated one-half full turn from the last. The transverse dimensions of this tubule are consistent with the ellipsoidal structures having a cross-section diameter of $\sim 0.7$ nm—roughly that of the diameter of $C_{60}$—observed by Wang and Buseck. In terms of a conformal mapping of a graphite sheet, this tubule structure is generated by mapping the line segment $OA$ in Figure 1 to the circumference of the tubule.

## ELECTRONIC STRUCTURE RESULTS

We have calculated the electronic structure of an infinitely long tubule using a first-principles, all-electron, self-consistent local-density functional (LDF) method originally developed to treat chain polymers [13] and recently adapted for helical symmetry. [14] This method calculates the total energy and the electronic structure using local Gaussian-type orbitals within a one-dimensional band structure approach. Our structure was generated by a planar ring of 10 carbon atoms with $D_{5h}$ symmetry arranged in 5 pairs; the distance between interior members of adjacent pairs was fixed at 0.284 nm, twice the nearest-neighbor separation typical of fullerenes and other graphitic systems. The tubule structure was generated with a screw operation having a twist of $\pi$ radians and a translational shift

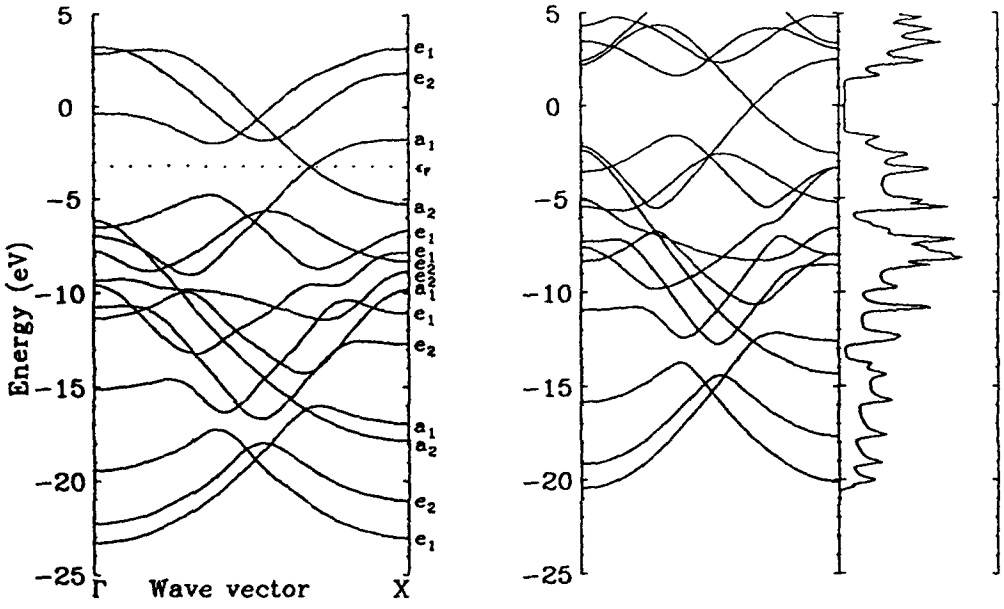


Figure 2. LDF (left) and valence tight-binding band structure and density-of-states (right, DOS is per carbon atom) for high-symmetry fullerene tubule. Note that the Fermi level is given by the dotted line denoted $\varepsilon_F$ for the LDF results and is defined at zero energy for the tight-binding results. DOS value at right-hand side of figure would be 0.8 $eV^{-1}$.

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of 0.123 nm chosen to yield nearest-neighbor separations between rings equal to the in-ring values. The one-electron states are Bloch functions generated by repeated application of the screw operation, and belong to irreducible representations of the screw symmetry group with a dimensionless analog of the wave vector, $k$. In the calculations we used 20 evenly-spaced points in the one-dimensional Brillouin zone ($-\pi < k \leq \pi$) and a carbon 7s3p Gaussian basis set.

We depict our calculated LDF valence band structure in the left-hand side of Figure 2. Because all of the operations of the $C_{5v}$ point group commute with the screw-symmetry space group, we label all bands according to the 4 irreducible representations of the $C_{5v}$ group: the rotationally-invariant $a_1$ and $a_2$ representations, and the doubly-degenerate $e_1$ and $e_2$ representations. Assignment of each calculated state to the appropriate symmetry then allows us to interpolate the bands to the resolution depicted in the figure. For this lattice structure we find the tubule is a metal, with the $a_1$ bands and $a_2$ bands crossing at a position in the Brillouin zone roughly 2/3 of the width of the half-Brillouin zone from the origin. The Fermi level, $\varepsilon_F$, coincides with this crossing.

We have also examined the use of an all-valence tight-binding model to calculate the electronic structure of larger tubule structures. We use a Slater-Koster parameterization [15] of the carbon valence states which we have parameterized [16,17] to earlier LDF band structure calculations [13] on polyacetylene. Within the notation of Ref. 15 our tight-binding parameters are given by $V_{ss\sigma} = -4.76$ eV, $V_{sp\sigma} = 4.33$ eV, $V_{pp\sigma} = 4.37$ eV, and $V_{pp\pi} = -2.77$ eV. We choose the diagonal term for the carbon $p$ orbital, $\varepsilon_p = 0$ which results in the $s$ diagonal term of $\varepsilon_s = -6.0$ eV. We see that this tight-binding model reproduces the LDF band structures qualitatively quite well. We note in the density-of-states that around the Fermi level this system behaves roughly as a metal with a nearly constant density-of-states. In other work [18] several of us have discussed the possibility that particular fullerene structures may have advantages over other conjugated carbon structures such as polyacetylene and over larger-diameter graphitic tubules. First, the coupling between electronic states and lattice should be such that no gap is introduced at $\varepsilon_F$ from Peierls distortion forces. [19] Second, a small diameter of the tubule should lead to an marked enhancement of carrier density in the tubule relative to that in normal

graphitic systems.

Iijima [7] has recently reported the preparation of graphitic tubules with diameters down to 2.2 nm. He interprets his electron diffraction data for these tubules as suggesting a range of tubule structures, including one example with one spiral rotation around the tubule axis giving an offset of three hexagons. Using the tight-binding model, we have examined a sample tubule which is generated by mapping the line segment $OB$ in Figure 1 to the circumference of the tubule. This structure can be described as a 6*222/7 helix, with 6 carbons per motif and 222 motifs and 7 helical turns over one translational period, with a diamter of ~2.5 nm. The tight-binding electronic structure and density-of-states of this tubule are depicted in Figure 3.

The dominant characteristic of the band structure in Figure 3 is the rapid oscillatory behavior of the energy levels as a function of wave vector. This wave vector $k$ is defined in terms of the phase shift of the local functions that comprise the Bloch functions for the delocalized states. The oscillatory behavior arises from hopping matrix elements between motifs which are close in real space but separated by a turn of the helix; the relative phase of these two functions thus oscillates rapidly as a function of $k$ leading to the observed behavior.

We note that the density-of-states is becoming markedly more like graphite than that for the smaller-diameter tubule described above. We see that this structure is also metallic (*i.e.*, no gap at $\varepsilon_F$) although this condition is not universally true for all helical structures. In addition, although this system also has a metallic density-of-states at $\varepsilon_F$, the magnitude has been reduced by roughly a factor of 4 compared to the smaller tubule. This factor, in conjunction with an increased volume per carbon atom, should lead to a reduction in the effective carrier density of roughly an order of magnitude compared to that expected for the smaller tubule.

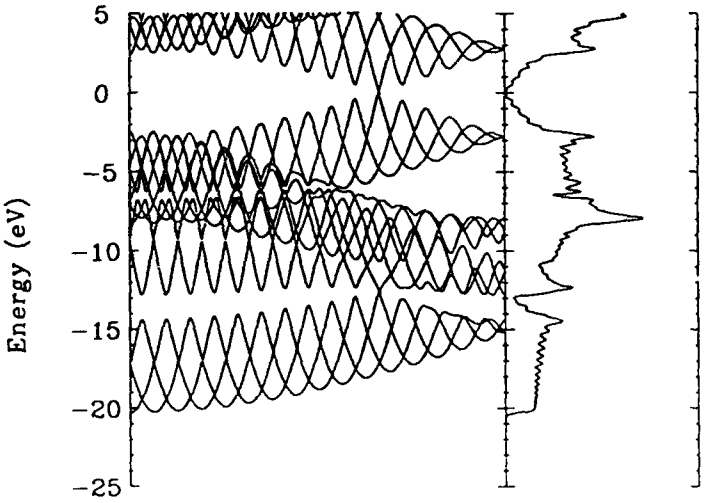


Figure 3. Valence tight-binding electronic band structure and density-of-states (per carbon atom) for 6*222/7 helix graphitic tubule. DOS scale is the same as in Figure 2.

## SUMMARY

We have presented results for the electronic structure of a high-symmetry fullerene tubule using a first-principles, self-consistent, all-electron Gaussian-orbital based local-density functional approach. Comparing these results for the high-symmetry tubule with a Slater-Koster tight-binding model, we find that the approach can give an reasonable

description of the electronic states with appropriate parameterization. We examined a tubule similar to those suggested by Iijima's work, and find that although closer in character to graphite than the smaller tubule, it can still have a metallic density-of-states at the Fermi level. In analyzing these example tubules we see that a relatively high carrier density could be expected for many of these structures.

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REFERENCES

1. W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Chem. Phys. Lett.* **170**, 167 (1990), *Nature* **347**, 354 (1990).
2. M. Dresselhaus and G. F. Dresselhaus, private communication.
3. S. Wang and P. R. Buseck, *Chem. Phys. Lett.* **181**, 1 (1991).
4. Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. Wang, J. M. Alford, and R. E. Smalley, *J. Phys. Chem.* **95**, 7564 (1991).
5. G. G. Tibbetts, *J. Crystal Growth* **66**, 632 (1984).
6. J. S. Speck, M. Endo, and M. S. Dresselhaus, *J. Crystal Growth* **94**, 834 (1989).
7. S. Iijima, *Nature* **354**, 56 (1991).
8. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature* **318**, 162 (1985).
9. R. Taylor, J. P. Hare, A. K. Abdul-Sada, and H. W. Kroto, *J. Chem. Soc., Chem. Commun.*, 1423 (1990).
10. R. D. Johnson, G. Meijer, and D. S. Bethune, *J. Am. Chem. Soc.* **112**, 8983 (1990).
11. H. Ajie, M. M Alvarez, S. J. Anz, R. D. Beck, F. Diederich, K. Fostiropoulos, D. R. Huffman, W. Krätschmer, Y. Rubin, K. E. Schriver, D. Sensharma, and R. L. Whetten, *J. Phys. Chem.* **94**, 8630 (1990).
12. R. D. Johnson, G. Meijer, J. R. Salem, and D. S. Bethune, *J. Am. Chem. Soc.* **113**, 3619 (1991).
13. J. W. Mintmire and C. T. White, *Phys. Rev. Lett.* **50**, 101 (1983); *Phys. Rev. B* **28**, 3283 (1983).
14. J. W. Mintmire, in *Density Functional Methods in Chemistry*, (Eds., J. Labanowski and J. Andzelm), pp. 125–138, Springer-Verlag (1991).
15. J. C. Slater and G. F. Koster, *Phys. Rev.* **94**, 1498 (1954).
16. M. L. Elert, J. W. Mintmire, and C. T. White, *J. Phys. (Paris), Colloq.* **44**, C3–451 (1983).
17. M. L. Elert, C. T. White, and J. W. Mintmire, *Mol. Cryst. Liq. Cryst.* **125**, 329 (1985).
18. J. W. Mintmire, B. I. Dunlap, and C. T. White, unpublished.
19. R. E. Peierls, *Quantum Theory of Solids* (Oxford Univ. Press, New York, 1955), p. 108.

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